V.N. Karazin Kharkiv National University

Medical Chemistry

Module 1. Lecture 3

Determination of the pH using indicators. Buffer solutions in an organism. Hydrolysis of salts. Colligative properties of solutions

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December, 15 2021

Lecture topics

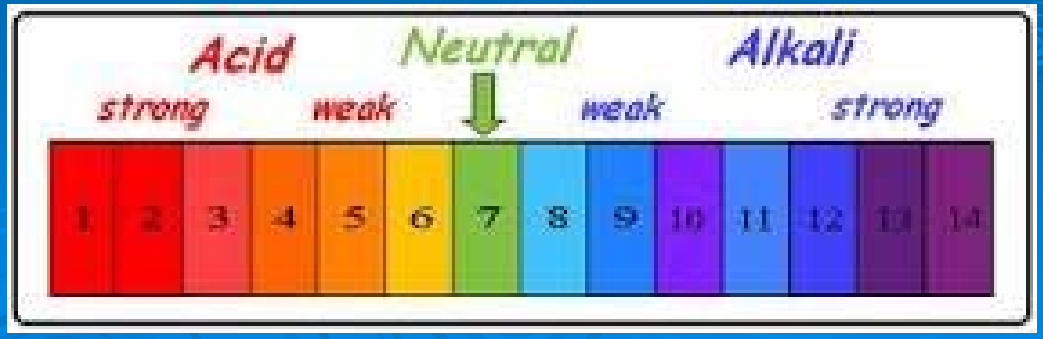
- √ Determination of the pH using indicators
- √ Buffer solutions in the organism
- √ Hydrolysis of salts
- √ Colligative properties of solutions:
  - Vapor pressure lowering
  - Boiling-point elevation
  - Freezing-point depression
  - Osmosis
- √ Colligative properties of electrolyte solutions

Determination of the pH using indicators

Due to the ability of indicators to change a color with pH of solution they are employed for determination of the acidity of solutions.

Universal indicator is a mixture of several indicators displaying a variety of colors over a wide pH range. Usually it is used as a *test paper* that changes color in accordance with the solution pH value.

Test papers of universal indicator are used only for an approximate pH of the solution. For precise determination of the pH value, *colorimetric* or *potentiometric methods* are used.



Buffer solutions in the organism

The pH of the blood plasma is maintained at about 7.40 by several buffer systems but the most important is the *bicarbonic buffer system*. This pH value is dependent upon two coupled reactions.

First, the equilibrium of gaseous carbon dioxide dissolved in the blood and water producing the carbonic acid:

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq).$$

The amount of carbon dioxide in the blood is coupled to the amount present in the lungs.

Second, the equilibrium between carbonic acid and bicarbonate ion:

$$H_2CO_3\ (aq) \leftrightarrow HCO_3^-\ (aq) + H^+\ (aq),\ pK = 6.37.$$

These reactions lead to the presence in solution the conjugate pair HCO_3^-/H_2CO_3 that forms the buffer system. The fact that the pH of normal blood is 7.40 implies that $[HCO_3^-]/[H_2CO_3] = 20$. The excess of an acid in the blood is fixed by interaction with hydrocarbonate ion, the excess of a base – by interaction with carbonic acid.

Buffer solutions in the organism

Hydrophosphate buffer system is formed by hydrophosphate and dihydrophosphate ions.

There is an protolytic equilibrium between these two ions:

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-},\ pK = 7.21.$$

If pH value of the blood is 7.40, the ratio of the concentrations of the ions $[HPO_4^{2-}]/[H_2PO_4^-]$ is 1.55 : 1.

Buffer solutions in the organism

In the erythrocytes the pH is 7.25, the principal buffer systems are bicarbonate HCO_3^-/H_2CO_3 and hemoglobin systems.

As a very rough approximation, we can treat it as a weak monoprotic acid of the form HHb that dissociates in solution:

$$HHb(aq) \leftrightarrow H^+(aq) + Hb^-(aq),$$

HHb represents the hemoglobin molecule and Hb^- the conjugate base of HHb. Oxyhemoglobin ($HHbO_2$), formed by the combination of oxygen with hemoglobin, is a stronger acid than HHb:

$$HHbO_2(aq) \leftrightarrow H^+(aq) + HbO_2^- (aq).$$

Hydrolysis of salts

The term ***salt hydrolysis*** describes *the reaction of an anion or a cation of a salt, or both, with water.* Salt hydrolysis usually affects the pH of a solution.

(1) *The salts composed of an alkali or alkaline earth metal ion and the residue of a strong acid do not undergo* hydrolysis and their solutions are assumed *to be neutral*.

(2) Another situation is observed when dissolved salt is formed by a *weak acid or (and) a weak base.*

For example, the dissociation of sodium acetate, that is strong electrolyte, in water proceeds according to equation: $CH_3COONa \rightarrow Na^+(aq) + CH_3COO^-(aq)$.

The sodium ion does not react with water. The acetate ion CH_3COO^- has an affinity for H^+ ions. The hydrolysis reaction of this anion is given by equation: $CH_3COO^-(aq) + H_2O \leftrightarrow CH_3COOH\ (aq) + OH^-\ (aq)$. Due to formation of OH^- ions in this reaction the solution of sodium acetate will be *basic*.

Hydrolysis of salts

The equilibrium constant for the hydrolysis reaction of CH_3COONa is determined by dissociation constant of acetic acid and ionic product of water:

$$K_h = \frac{[CH_3COOH]\cdot[HO^-]}{[CH_3COO^-]} = \frac{K_w}{K_{acid}}$$

(3) When a salt derived from a strong acid and a weak base dissolves in water, the solution becomes *acidic*.

For example, in solution of NH_4Cl the dissociation process gives NH_4^+ and Cl^- ions: $NH_4Cl \rightarrow NH_4^+(aq) + Cl^-(aq)$.

The ammonium ion NH_4^+ is the conjugate acid of the weak base NH_3 and reacts with water molecule: $NH_4^+(aq) + H_2O \leftrightarrow NH_3(aq) + H_3O^+(aq)$.

Because this reaction produces H_3O^+ ions, the pH of the solution decreases. The equilibrium constant (hydrolysis constant) for this process is given by equation:

$$K_h = \frac{[NH_3]\cdot[H_3O^+]}{[NH_4^+]} = \frac{K_w}{K_{base}}$$

Hydrolysis of salts

(4) For salts formed by a weak acid and a weak base, both the cation and the anion hydrolyze. The hydrolysis constant in this case is determined by both dissociation constants of the acid and the base:

$$K_h = \frac{K_w}{K_{acid} \cdot K_{base}}$$

If $K_{base} > K_{acid}$ then the solution must be basic because the anion will hydrolyze to a greater extent than the cation. At equilibrium, there will be more OH^- ions than H^+ ions.

If K_{base} for the anion is smaller than K_{acid} for the cation, the solution will be acidic because cation hydrolysis will be more extensive than anion hydrolysis.

If K_{base} is approximately equal to K_{acid}, the solution *will be nearly neutral*.

Colligative properties of solutions

*Colligative properties of solutions are several important properties that depend on the number of solute particles (*atoms, ions or molecules*) in solution and not on the nature of the solute particles.*

It is important to keep in mind that we are talking about relatively dilute solutions, that is, solutions whose concentrations are less 0.1 mol/L.

The term “colligative properties” denotes “properties that depend on the collection”.

The colligative properties are:

- vapor pressure lowering,
- boiling-point elevation,
- freezing-point depression,
- osmotic pressure.

Colligative properties of solutions: Vapor pressure lowering

If a solute is *nonvolatile,* **vapor pressure of the solution is always less than that of the pure solvent** and depends on the concentration of the solute.

The relationship between solution vapor pressure and solvent vapor pressure is known as *Raoult's law*.

This law states that *the vapor pressure of a solvent over a solution* (p_1) *equals the product of vapor pressure of the pure solvent* ($p_1°$) *and the mole fraction of the solvent in the solution* (x_1):

$$p_1 = x_1 p_1°.$$

Colligative properties of solutions: Vapor pressure lowering

In a solution containing only one solute, than $x_1 = 1 - x_2$, where x_2 is the mole fraction of the solute.

Equation of the Raoult's law can therefore be rewritten as

$$(p_1^\circ - p_1)/p_1^\circ = x_2.$$

One can see that the *relative decrease in vapor pressure* of the solvent is *directly proportional to the mole fraction of the solute in solution*.

Colligative properties of solutions: Boiling-point elevation

The boiling of a pure liquid or a solution occurs at that temperature at which its vapor pressure becomes equal the external atmospheric pressure.

Because at any temperature the vapor pressure of the solution is lower than that of the pure solvent, the vapor pressure of solution reaches atmospheric pressure at a higher temperature than the normal boiling point of the pure solvent.

This leads to *elevation of boiling point* of solution in comparison with pure solvent. The *boiling-point elevation* is defined as:

$$\Delta T_b = T_b - T_{b,o} > 0$$

where T_b is the boiling point of the solution, $T_{b,o}$ – the boiling point of the pure solvent.

Colligative properties of solutions: Boiling-point elevation

$$\Delta T_b = K_b m,$$

where m – molality of the solute, K_b is the *molal boiling-point elevation constant.*

It has been proved theoretically that K_b is determined only by properties of the solvent:

$$K_b = \frac{RT_{b,o}^2 \cdot M_1}{1000 \cdot \Delta H_{vap}^o}$$

R – universal gas constant, M_1 – molar mass of the solvent, $\Delta H°_{vap}$ – enthalpy change of vaporization of the pure solvent.

The value of boiling-point elevation constant for water is 0.52 K·kg/mol. One can see that if the molality of an aqueous solution is 1.00 mol/kg, the boiling point will be 100.52 °C.

Colligative properties of solutions: Freezing-point depression

The pure solvent freezes if its vapor pressures in liquid and solid states are equal. The vapor pressure of a solid solvent depends on temperature only and decreases with decrease in temperature.

These leads the temperature of the freezing of solution is *lower* than the freezing point of the solvent. The *depression of freezing point* is defined as:

$$\Delta T_f = T_{o,f} - T_f > 0$$

$T_{o,f}$ – freezing point of the pure solvent, and T_f – freezing point of the solution. The ΔT_f value is proportional to the molal concentration of the solute:

$$\Delta T_f = K_f m,$$

where m – molality of the solute, and K_f is the *molal freezing-point depression constant*. Like K_b, the K_f has the units $K \cdot kg \cdot mol^{-1}$.

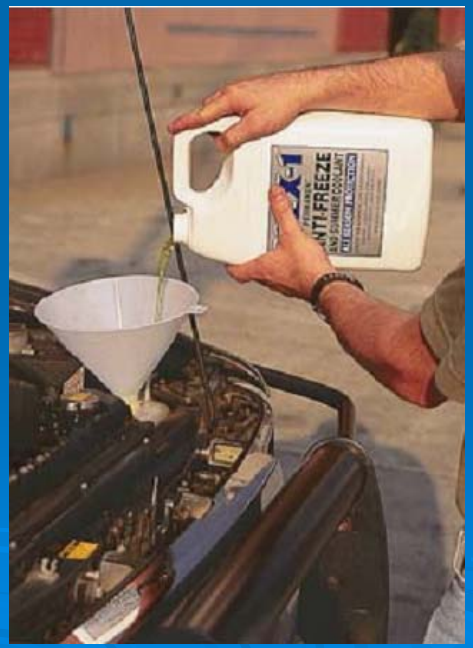
Colligative properties of solutions: Freezing-point depression

The K_f value depends only on properties of the solvent:

$$K_f = \frac{RT_{f,o}^2 \cdot M_1}{1000 \cdot \Delta H_{fus}^o}$$

ΔH_{fus} is enthalpy change of fusion of the pure solvent.

De-icing of airplanes is based on freezing-point depression



In cold climate regions, antifreeze must be used in car radiators in winter

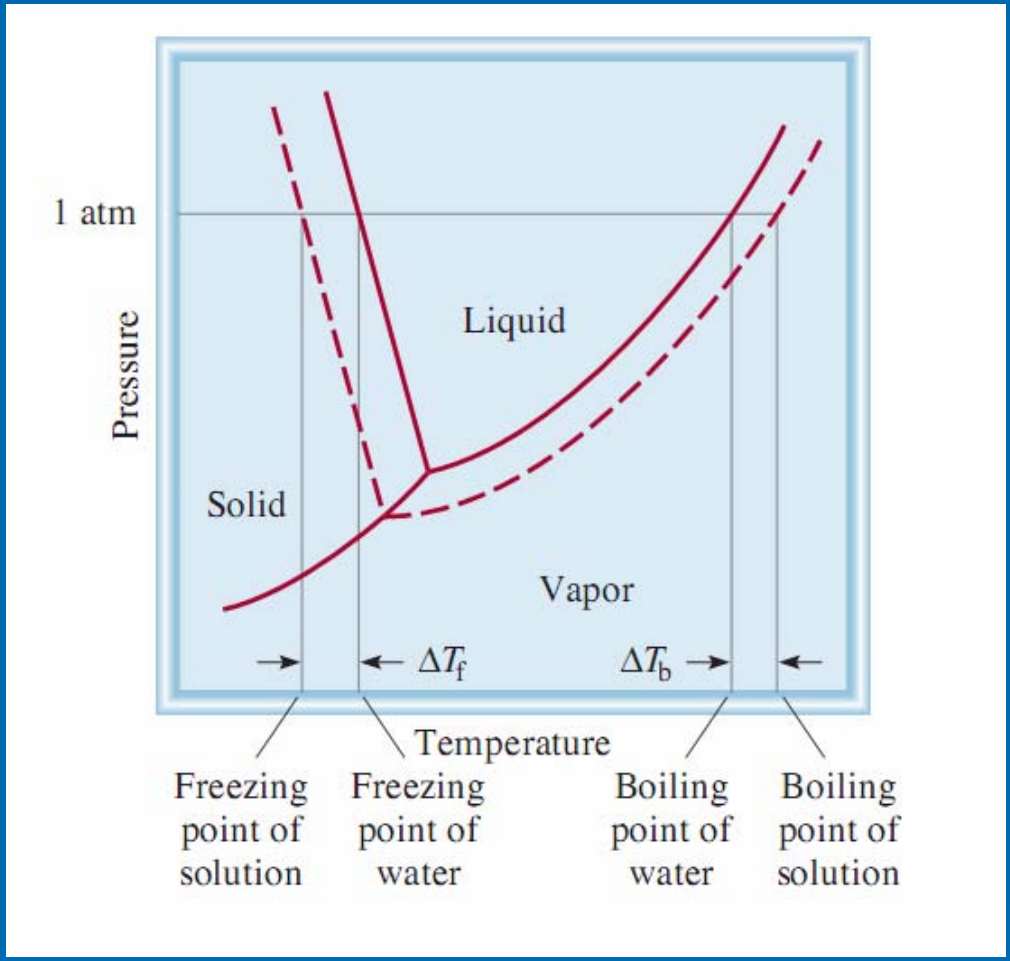


Figure. Phase diagram illustrating the boiling-point elevation and freezing-point depression of aqueous solutions.

The dashed curves pertain to the solution, and the solid curves to the pure solvent. As you can see, the boiling point of the solution is higher than that of water, and the freezing point of the solution is lower than that of water

Colligative properties of solutions: Freezing-point depression and Boiling-point elevation

Table lists values of K_b for several common solvents. You can see that if the molality of an aqueous solution is 1.00 m, the boiling point will be 100.52°C.

Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

Solvent	Normal Freezing Point (°C)*	K_f (°C/*m*)	Normal Boiling Point (°C)*	K_b (°C/*m*)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	−117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

*Measured at 1 atm.

Colligative properties of solutions: Osmosis

Osmosis is the spontaneous movement of a pure solvent into a solution separated from it by a semipermeable membrane.

The membrane is permeable by the solvent molecules but not by the solute and allows the solvent, but not the solute, to pass through.

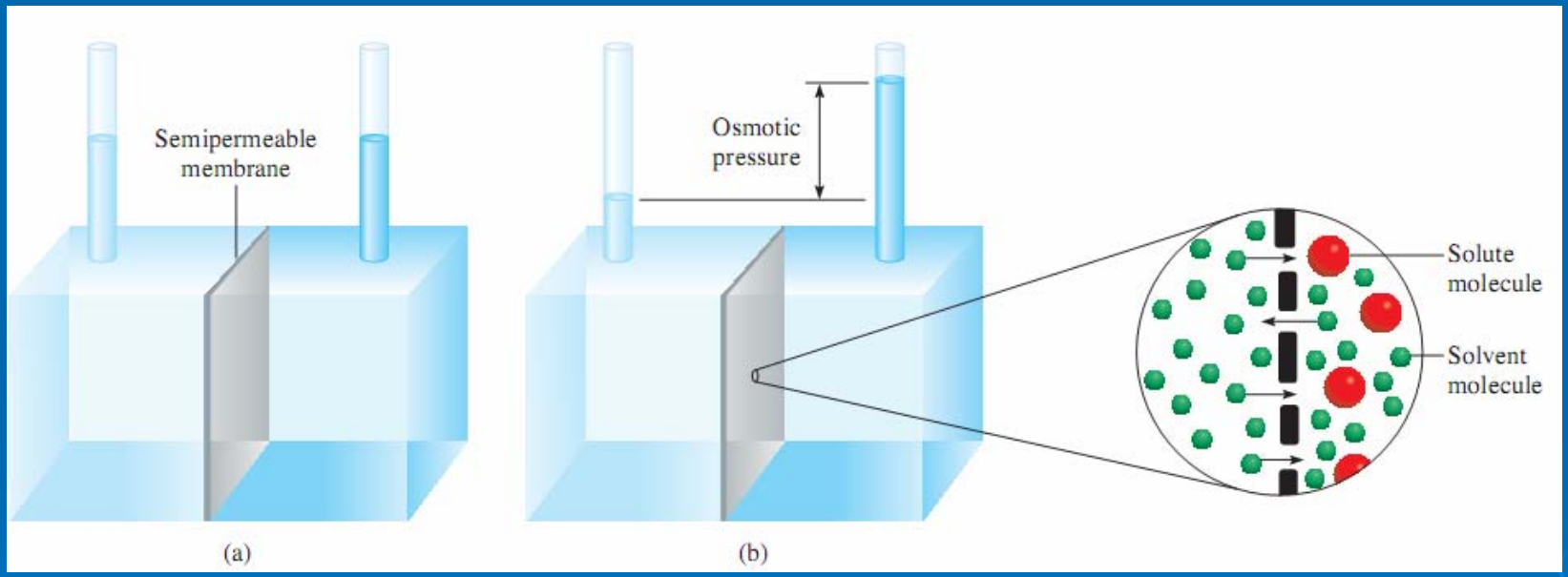


Figure. Osmotic pressure. (a) The levels of the pure solvent (left) and of the solution (right) are equal at the start. (b) During osmosis, the level on the solution side rises as a result of the net flow of solvent from left to right. The osmotic pressure is equal to the hydrostatic pressure exerted by the column of fluid in the right tube at equilibrium

Colligative properties of solutions: Osmosis

The osmotic pressure *is the pressure that must be applied to the solution to prevent the solvent transfer*.

For dilute solutions the osmotic pressure is given by the van't Hoff equation:

$$\pi = cRT,$$

T – absolute temperature, *c* – molar concentration of the solute, *R* − universal gas constant.

If two solutions are of equal concentration and, hence, of the same osmotic pressure, they are said to be *isotonic*.

If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be *hypertonic* and the more dilute solution is described as *hypotonic*.

Colligative properties of solutions: Osmosis

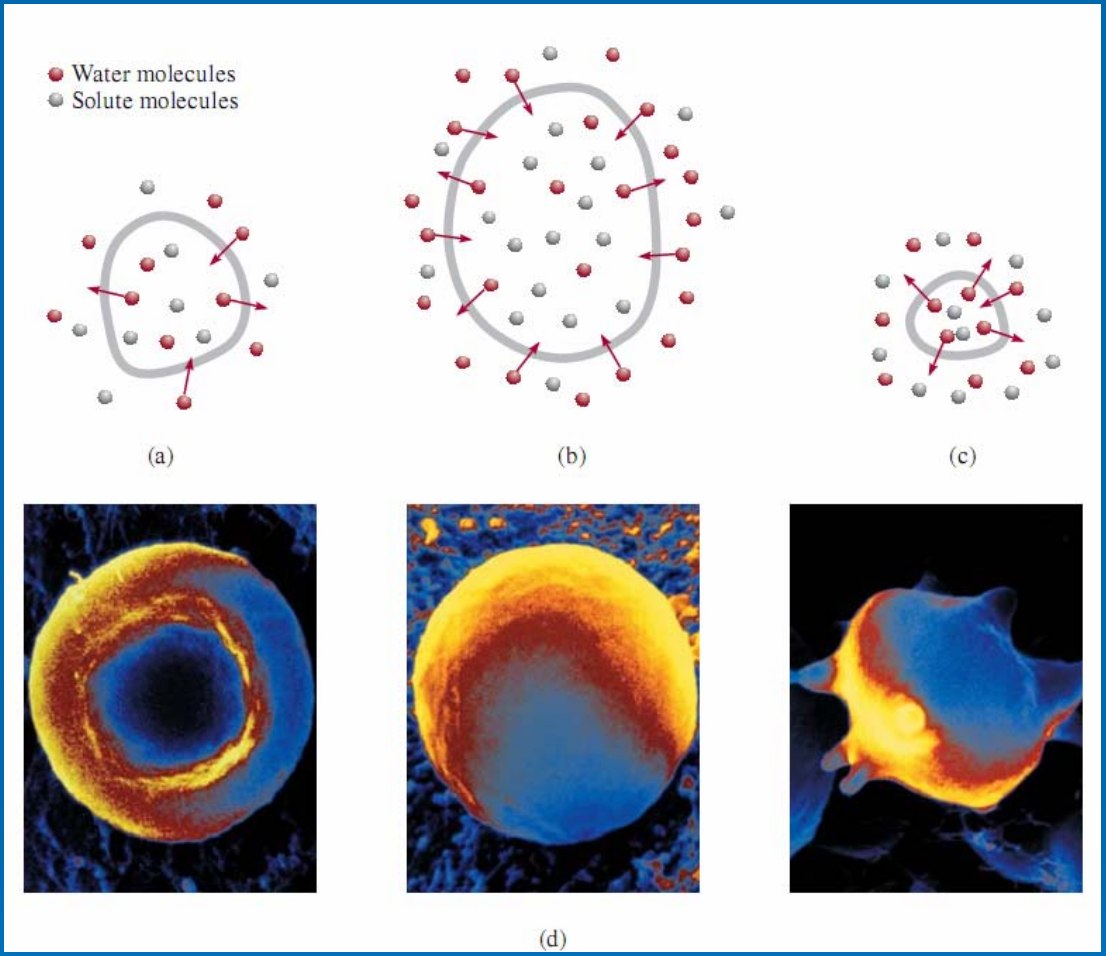


Figure. A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b), and shrinks in (c). (d) From left to right: a red blood cell in an isotonic solution, in a hypotonic solution, and in a hypertonic solution.

Colligative properties of electrolyte solutions

The colligative properties of electrolytes is characterized by slightly different approach than the one used for the colligative properties of nonelectrolytes.

The colligative properties of binary electrolyte solution should be twice as great as those of an electrolyte solution containing a nonelectrolyte in the same concentration. Similarly, we would expect a ternary electrolyte solution to depress the freezing point by three times as much as a nonelectrolyte solution with the concentration. *To account for this effect we must modify the equations for colligative properties as follows*:

- $\Delta T_b = iK_b \cdot m,$
- $(p_1^\circ - p_1)/p_1^\circ = ix_2,$
- $\Delta T_f = iK_f \cdot m,$
- $\pi = icRT.$

Colligative properties of electrolyte solutions

The variable *i is the van't Hoff's isotonic factor*, which is defined as the ratio of actual number of particles in solution after dissociation and number of molecules (structural units) of initially dissolved substance.

$$i = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}$$

Thus, i should be 1 for nonelectrolytes. For strong binary electrolytes such as NaCl and KNO_3, should be 2, and for strong ternary electrolytes such as Na_2SO_4 and $MgCl_2$, *i* should be 3.

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